

INTERLABORATORY
STUDY 92-3

ORGANOCHLORINE
PESTICIDE
(OC's)
STANDARD
SOLUTIONS

IN SUPPORT OF
THE INTEGRATED
ATMOSPHERIC
DEPOSITION
NETWORK
(IADN)

OCTOBER 1992



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for

**Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy**

and

**Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report: 93-13**

The author gratefully acknowledges and thanks Lloyd Winfield for the preparation of materials, Patrick Crozier, Angelo Alfieri and Gerry Ladwig for the confirmation of concentrations, and Don King, Sathi Selliah, Renata Baily, Syed Iqbal, and Robert Vet for their help in reviewing the results.

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1 SUMMARY OF INTERLABORATORY STUDY 92-3

Interlaboratory Study 92-3 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of laboratory variability for the analysis of Organochlorine Pesticides (OC's). Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 18 different OC's. All 18 compounds were present in each ampoule at four different concentrations.

The results of this interlaboratory study indicate that the participants have an agreement of $\pm 20\%$ to the target for most parameters. The within-laboratory performance tends to be consistent across the concentration range, though some participants were erratic for some parameters. Slope problems are the most common source of between-laboratory variability. As between-participant bias may be as high as 30-40%, the use of a common reference standard could help reduce this bias range to $< 10-15\%$. This would reduce the potential bias from the contributing laboratories to the central IADN database.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission¹. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan². This interlaboratory study provides information on the laboratory component of between agency differences, and can be used to help establish the comparability of the data sets. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 92-3 targets laboratories analyzing for Organochlorine Pesticides (OC's) in precipitation and/or ambient air. A target list of 18 OC's was chosen for this study, comprising target lists from several contributing agencies. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of ampouled standards ready for direct instrumental analysis. Each ampoule contained all of the parameters in the target list.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat OC's of 99% + purity were purchased from Ultra Scientific and Supelco by AES. All subsequent work was done by the QMU of LSB, MOEE. Three concentrated stock solutions containing six compounds each were prepared in 2% toluene/iso-octane, and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 15 mg/L and verified using gas chromatography/electron capture detector (GC/ECD) analysis by an analytical unit at LSB not involved in analysis of ambient air or precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for the interlaboratory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution in iso-octane. Concentrations were chosen to span the routine instrumental calibration range of the participants. The solutions were sealed in 5 mL amber ampoules and labelled IADN OC1, IADN OC2, IADN OC3, and IADN OC4. (Further reference to these ampoules eliminates "IADN".) All ampoules were stored in a freezer at -20°C until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on October 5, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the solutions using their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program. The solutions were ready for direct instrumental injection and participants were asked not to do any sample preparation steps. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument and Detector used for the analysis. Information regarding the gas chromatograph column was requested at a later date. All participants were assigned a unique identification code that does not correspond to the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on January 15, 1993. Three participants submitted revisions to some of their results. For all of these participants, both sets of results are included in the tables. Their comments are noted as foot-notes to the tables and discussed in the individual laboratory review.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each parameter in each of the ampoules for which there were 2 or more results reported, and are included in Tables 1-4, Appendix 1. For p,p-DDD in Ampoule OC2, Laboratory 9236's result was excluded from the calculation of the interlaboratory mean, median, SD and %RSD. The explanation for this is given in the individual review of this participant's results in section 4.

The results for each participant were also plotted to facilitate interpretation of the interlaboratory performance. The results for each parameter are plotted as a difference from the target versus concentration, both as an absolute value (ng/mL) and as a percentage difference from the target. These figures are all included in Appendix 1.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from all of the participants who received the ampouled solutions. Qualifying remarks from the participants are provided in the individual laboratory review below. A description of the principles upon which the following discussion is based is provided in Appendix 3.

The results for α -Hexachlorocyclohexane (α -HCH) in Figure 1 demonstrate a negative slope bias among the participants. Only Laboratory 9236 had a positive slope. All of the participants except Laboratory 9236 agreed with each other within $\pm 10\%$ at the higher concentrations (Figure 2). However they are biased low relative to the target, except for Laboratory 9236's result for OC2.

The γ -Hexachlorocyclohexane (γ -HCH) results (Figure 3) indicate a negative slope bias. All of the participants agreed with each other within a range of 1-2.5 ng/mL across the concentration range, but were low relative to the target. At the higher concentrations, this range of agreement is within 15% (Figure 4).

The majority of participants have good agreement with the target and each other for p,p-DDT (Figures 5 and 6). Laboratory 9232 was erratic and Laboratory 9236 has a negative slope bias.

The results for o,p-DDT (Figure 7) demonstrate very good agreement with the target and among the participants. Laboratory 9234 appears to have a slight negative slope problem. There may be a slight degree of curvature at the highest concentration, as many of the participants have a positive difference from the target for samples OC3 and OC4, but then have a slight negative difference from the target for OC2. The overall between laboratory variability is 20%, except for Laboratory 9232 in Ampoule OC1.

All of the participants' results for p,p-DDD are plotted in Figures 9 and 10, but a second set of graphs with Laboratory 9236 excluded are also presented in Figures 11 and 12. See individual discussion below for an explanation of Laboratory 9236's results for p,p-DDD. The majority of the other participants demonstrate good agreement with the target and with each other for p,p-DDD (Figure 11). Laboratory 9234 has a negative slope problem. The range of results between the participants is approximately 20% (Figure 12).

The p,p-DDE results (Figure 13) demonstrate consistent performance across the concentration range for most participants, with generally good agreement with the target. Laboratory 9233-V was biased high. Laboratories 9234 and 9236 have a negative slope problem. Excluding Laboratory 9233-V, and Laboratory 9236 for Ampoules OC1 and OC2, the between laboratory variability is approximately 20% (Figure 14).

The majority of the participants reported results for α -Chlordane that differed from the target by approximately -10%. This was consistent across the analytical range (Figure 15). Agreement among the participants was within a range of approximately 10%, except for Laboratory 9234 in Ampoules OC4 and OC1 (Figure 16). Laboratory 9234 has a negative slope problem.

The results for γ -Chlordane (Figure 17) demonstrate consistent performance by all of the participants across the analytical range, except for Laboratory 9234. The consensus among the participants suggests a -5% difference from the target, with a range of 10% among the majority of participants, except for Laboratory 9234 (Figure 18). For most programs, this degree of variability is better than expected.

Laboratories 9233-V and 9234 did not report a positive response for the lowest concentration of Heptachlor Epoxide (Ampoule OC1, Table 1). This may have been below these participants' detection limit for this parameter. Agreement was very good among the participants and with the target value for Heptachlor Epoxide (Figure 19). Laboratory 9234 was erratic for this parameter. Excluding Laboratory 9234, the between laboratory variability was 10-15% (Figure 20).

Most participants demonstrated consistent performance across the concentration range for Methoxychlor (Figure 21). Laboratory 9234 was biased high. Laboratory 9232 was erratic and may have a curvature problem at the higher concentration level. Excluding Laboratory 9234, and Laboratory 9232 for Ampoule OC3, the between laboratory variability was approximately 25% (Figure 22).

The Dieldrin results (Figures 23 and 24) demonstrate consistent performance across the concentration range by most participants. There is a between-laboratory range of approximately 30%. Laboratory 9231 was biased slightly high compared to the other participants. Laboratory 9236 has a slight negative slope problem.

For Hexachlorobenzene (HCB), Laboratory 9236 has a high positive slope bias and Laboratory 9234 has a large negative slope bias. The other participants demonstrate consistent performance across the analytical range and acceptable agreement with the target (Figure 25). The overall results demonstrate a between-laboratory range of 40% (Figure 26).

Most participants demonstrated consistent performance across the concentration range for Endosulfan I (Figure 27). Laboratory 9233-HP may have a curvature problem at the highest concentration level. Laboratory 9234 is biased high and may also have an intercept problem. The between-laboratory range is approximately 20% (Figure 28), excluding Laboratory 9234 for OC2 and OC1, and Laboratory 9233-HP for OC4.

The Endosulfan II results show consistent performance across the concentration range (Figure 29) except for Laboratory 9231. There is a slight drop at the higher concentration levels (OC4 and OC2) which may indicate some curvature. Laboratory 9231 has a positive slope bias. The between-laboratory range, excluding Laboratory 9231, is approximately 10-15% (Figure 30).

Graphs were not plotted for those parameters with less than five sets of results. Only Laboratory 9234 reported results for o,p-DDE. They were low relative to the target with a possible negative slope (Tables 1-4).

Only three participants reported results for o,p-DDD. Agreement with the target and each other was good at the lower concentrations (Tables 2-4), but all three laboratories were biased low at the highest concentration (Table 1), suggesting a slope problem.

Four laboratories reported results for Endrin. Two laboratories were high and two were low (Tables 1, 2 and 4), indicating no consensus among the participants or agreement with the target. Endrin is part of the secondary list of target parameters for the IADN program². These results indicate that the use of a reference standard to validate the

accuracy of calibration standards is particularly important for the laboratories contributing Endrin data to the central IADN database.

Four laboratories reported results for Oxychlordane. All the results were low relative to the target value (Tables 1-4). Laboratory 9234 was erratic, as they had a positive result for the lowest concentration sample (OC3) but reported "ND" for the second concentration level (OC2).

The main source of between-laboratory variability appears to be slope bias. This may be corrected with the use of a reference standard by all participants contributing to the central IADN database, as mentioned above for Endrin. Temperature programming conditions, gas flow rates, detector differences, and software integration differences are some of the other possible sources of variation between the participants. While all the participants used a DB-5 capillary column as one of their analytical columns (Table 5), there were differences in column length (30 m or 60 m) that may also contribute to variability among the participants, due to the presence of co-eluters or poor resolution between analytical peaks.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9231

Laboratory 9231 noted with their results that they routinely analyze samples for OC's using a DB-5 column. A second injection was done using a DB-17 column for confirmation for those parameters that had non-optimal resolution on the DB-5 column. Those parameters were o,p-DDD, Heptachlor Epoxide, Dieldrin, and Oxychlordane. They did not indicate whether this was a routine procedure that would be used for samples.

They had very good agreement with the target for most parameters. They were biased low for α -HCH and γ -HCH. They had a high slope bias for Dieldrin and Endosulfan II, though they were within 10-15% of the target.

Laboratory 9232

Laboratory 9232 demonstrated erratic performance for p,p-DDT, o,p-DDT, and Methoxychlor. They should investigate their instrumental conditions with respect to these three parameters. Performance was consistent for the other parameters in this study. They generally had good agreement with the target, with some slight high or low slope biases for a few parameters.

Laboratory 9233

Laboratory 9233 analyzed the solutions using two different instruments. Their results are marked "-HP" and "-V" in Tables 1-4 to correspond with the two systems listed in Table 5. When they received the original table of results, they questioned their own results for Heptachlor Epoxide, Hexachlorobenzene, and Oxychlordane, particularly in regards to the age of their own calibration standard. A new calibration standard was immediately prepared, and when compared to their old standard, they noted the differences for the above three parameters. They re-analyzed the interlaboratory study solutions and submitted revised results for the above three compounds, though the same values were obtained for Heptachlor Epoxide using the Varian system. The

original results are enclosed in brackets in the tables of results, with the revised results being used for the statistical calculations and the graphs.

The results using the HP system demonstrated consistent performance across the concentration range for all parameters except Endosulfan I. They may have a curvature problem at the highest concentration level in this study, as they reported a much lower result for ampoule OC4 than the target (Figure 27).

The results using the Varian system also demonstrated consistent performance across the concentration range except for p,p-DDE and Heptachlor Epoxide. The results for p,p-DDE (Figure 13) indicate a high slope bias. Using the Varian system, Laboratory 9233 did not report a positive response for Heptachlor Epoxide in OC1. This suggests that this analytical system is not as sensitive for Heptachlor Epoxide but the Varian system had only a 5% difference from target at higher concentrations (Figure 20).

The results from the HP system were 10% lower than the results from the Varian system for the majority of parameters. As seen in Table 6 and Figure 31, there was a greater percentage of results from the Varian in the range 90-110% and 110-130% of target than for the HP system. Laboratory 9233 used the same calibration standard and the same type of capillary columns on both instrumental systems, it appears that the differences in the two sets of results are instrument related. Temperature programming conditions, gas flow rates, detector differences, and software integration differences are some of the possible sources of variation between the two data sets. Laboratory 9233 should do further investigations to resolve these differences so that they can report a consistent data set using either analytical system.

Laboratory 9234

Laboratory 9234 originally analyzed the solutions using a new Varian 3400 with a Septum Programmable Injector (SPI). When they received the original table of results, they investigated the possible sources of their discrepancies from the target and determined that the SPI was the source of their differences. They reanalysed the solutions using their older Vista 6000 with a split/splitless injector, and submitted a revised data set, requesting that the original data set be withdrawn. The original data set is included in Tables 1-4 and is marked with an asterisk. The revised data set was used for the statistical calculations and the graphs.

Laboratory 9234 had a negative slope problem and was biased low for most parameters. Their performance for Heptachlor Epoxide and Oxychlorane was erratic. For Heptachlor Epoxide at the low concentration (OC1) they reported "ND", while at the higher concentrations both positive and negative differences from the target were observed. For Oxychlorane, a "ND" was reported for a target value of 7.30 ng/mL (OC2), but a value of 2.54 ng/mL was reported for OC3 that had a target value of 3.65. They had a high positive slope problem for Methoxychlor and Endosulfan I. Only for p,p-DDT did they demonstrate good performance across the concentration range with no slope problems and good agreement with the target. Verification of their standards with a common reference standard should improve Laboratory 9234's agreement with the other participants and the target.

Laboratory 9235

Laboratory 9235's results were the most consistent with the target and the most consistent in the centre of the range among the participants (Table 6 and displayed in

Figure 31). Only for Endosulfan II did they report the lowest results among the participants, but they differed from the target by only -10%.

Laboratory 9236

Laboratory 9236 provided revisions to their results after receiving the original tables of results. They reviewed their quantitation of α -HCH and found an error. They requantitated the chromatograph and provided revised results. The revised α -HCH results were used in the statistical calculations and graphs, with the original results included in Tables 1-4 in brackets.

They also noted that in their analytical system, p,p-DDD (on their target list) co-elutes with o,p-DDT (not on their target list). As their results were high for p,p-DDD, they attributed their bias to the co-elution of o,p-DDT. They subtracted the target value of o,p-DDT from their reported p,p-DDD value and submitted revised results. The original p,p-DDD results are retained as part of the data set, with the "corrected" results in square brackets. In a sample, this laboratory would not know that a peak identified as p,p-DDD could also include o,p-DDT unless they had a separate calibration standard. For unknown samples, they would be unable to subtract a "target value" of a co-eluting compound, so it would be inappropriate to do so for the interlaboratory study solutions. As seen in Table 2, their result for p,p-DDD in Ampoule OC2 was particularly biased high by this co-elution effect. Laboratory 9236's OC2 value has been excluded from the statistical calculations for p,p-DDD results as it is an obvious outlier.

Laboratory 9236 had a negative slope problem and were biased low for p,p-DDT, p,p-DDE and Dieldrin. They had the reverse problem for Hexachlorobenzene and α -HCH, for which they had a positive slope problem. They demonstrated consistent performance for γ -HCH and Dieldrin.

5 CONCLUSION

The results of this interlaboratory study indicate that the participants have an agreement of $\pm 20\%$ to the target for most parameters. The within-laboratory performance tends to be consistent across the concentration range, though some participants were erratic for some parameters. Slope problems are the most common source of between-laboratory variability. As between-participant bias may be as high as 30-40%, the use of a common reference standard could help improve this bias to 10-15%. This would reduce the potential bias from the contributing laboratories to the central IADN database.

6 REFERENCES

1. International Joint Commission, United States and Canada; January 1988. *Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed November 18, 1987.*
2. Canada/U.S. Coordinating Committee on Annex 15; March 1990. *Integrated Atmospheric Deposition Network Implementation Plan.*
3. *Integrated Atmospheric Deposition Network "STRAW MAN" Quality Assurance Program Plan (DRAFT); November 1992.*

7 APPENDIX 1 - RESULTS AND GRAPHS

Table 1	Ampoule IADN OC1
Table 2	Ampoule IADN OC2
Table 3	Ampoule IADN OC3
Table 4	Ampoule IADN OC4
Table 5	Instruments and GC Columns
Table 6	Distribution of Participants' Results Relative to Target
Figures 1 - 30	Difference from Target Plots
Figure 31	Distribution of Participants' Results Relative to Target

TABLE 1 - Results for IADN OC1 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
α-HCH	2.58	1.32	2.88	1.6	2.2	2.46	2.1	2.28 (0.537)	2.11	2.2	0.516	7	24.42%	2.35
γ-HCH	15.60	13.81	12.88	12.4	14.1	12.19	13.2	13.793	13.20	13.2	0.741	7	5.62%	10.15
p,p-DDT	4.80	4.37	3.60	4.4	4.6	5.13	5.0	4.628	4.53	4.6	0.500	7	11.04%	2.94
o,p-DDT	2.40	2.38	1.90	2.4	2.6	2.53	2.2	N/A	2.33	2.38	0.253	6	10.66%	1.94
p,p-DDD	5.95	5.91	6.83	5.0	5.8	6.09	5.0	9.082 (6.68)	6.24	5.81	1.404	7	22.48%	ND
o,p-DDD	18.80	14.28	12.85	N/A	N/A	14.45	N/A	N/A	13.88	14.28	0.879	3	6.34%	11.38
p,p-DDE	2.55	2.33	2.22	2.2	3.0	3.72	2.3	3.1685	2.71	2.33	0.595	7	22.01%	ND
o,p-DDE	6.05	N/A	N/A	N/A	N/A	5.26	N/A	N/A	-	-	-	1	-	4.17
α-Chlordane	17.10	16.15	14.14	15.0	15.4	13.70	15.5	N/A	14.88	15.2	0.812	6	6.09%	10.28
γ-Chlordane	5.50	5.07	5.38	4.9	5.1	5.27	5.2	N/A	5.15	5.15	0.168	6	3.26%	3.81
Heptachlor Epoxide	2.55	2.69	2.75	2.5 (ND)	ND	ND	2.5	N/A	1.74	2.5	1.352	6	77.67%	ND
p,p-Methoxychlor	14.70	15.97	10.08	11.4	14.3	19.62	12.7	N/A	14.05	13.5	3.511	6	25.00%	8.20
Dieldrin	5.40	6.11	5.01	4.7	5.4	4.82	4.8	5.875	5.19	5.01	0.560	7	10.80%	5.13
Hexachlorobenzene	2.65	2.19	2.48	2.8 (0.8)	3.1 (0.9)	2.57	2.7	2.941	2.68	2.7	0.305	7	11.40%	1.88
Endrin	16.80	26.00	13.39	N/A	N/A	20.81	13.8	N/A	18.40	17.105	6.077	4	33.03%	12.97
Endosulfan I	5.80	4.83	5.55	5.7	6.5	7.74	5.1	N/A	5.80	5.625	1.067	6	18.08%	7.53
Endosulfan II	2.53	2.81	2.48	2.4	2.7	N/A	2.3	N/A	2.54	2.48	0.212	5	8.34%	N/A
Oxychlordane	21.90	19.42	N/A	18.0 (ND)	19.8 (45.3)	21.13	N/A	N/A	19.54	19.51	1.280	4	6.55%	20.00

TABLE 2 - Results for IADN OC2 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
α-HCH	15.11	12.52	13.70	11.4	13.0	12.17	12.9	16.67 (3.9585)	13.19	12.9	1.692	7	12.83%	13.25
γ-HCH	5.20	3.33	5.04	3.8	4.7	4.37	4.5	4.5785	4.33	4.5	0.579	7	13.38%	3.74
p,p-DDT	2.40	2.17	2.77	2.3	2.4	2.92	2.8	1.942	2.44	2.4	0.343	7	14.05%	1.54
o,p-DDT	14.40	13.78	13.31	13.7	14.0	11.80	14.5	N/A	13.52	13.74	0.927	6	6.86%	7.87
p,p-DDD	2.98	3.06	3.51	2.7	3.0	3.55	2.5	17.829 # [3.43]	3.50	3.06	0.422	6	13.81%	2.20
o,p-DDD	6.30	5.52	7.12	N/A	N/A	5.55	N/A	N/A	6.06	5.55	0.815	3	15.09%	4.51
p,p-DDE	15.30	14.87	14.06	14.4	18.6	12.19	13.5	15.041	14.67	14.4	1.983	7	13.52%	9.33
o,p-DDE	3.03	N/A	N/A	N/A	N/A	2.62	N/A	N/A	-	-	-	1	-	2.13
α-Chlordane	5.70	5.01	5.31	5.0	5.3	5.19	5.2	N/A	5.17	5.195	0.138	6	2.63%	3.65
γ-Chlordane	2.75	2.51	3.00	2.8	2.8	2.80	2.7	N/A	2.70	2.65	0.177	6	6.54%	1.98
Heptachlor Epoxide	15.30	15.19	14.85	14.8 (14.9)	15.8	18.85	15.2	N/A	15.42	15.195	0.760	6	4.93%	13.61
p,p-Methoxychlor	4.90	5.09	5.32	4.8	4.8	7.38	5.1	N/A	5.35	5.095	1.029	6	19.25%	3.88
Dieldrin	2.70	3.03	2.39	2.5	2.5	2.49	2.5	2.9585	2.82	2.5	0.258	7	9.77%	2.13
Hexachlorobenzene	15.90	14.59	13.06	17.1 (5.0)	17.7 (5.2)	11.82	18.2	20.22	15.78	18.2	2.928	7	18.55%	10.78
Endrin	5.80	8.23	5.44	N/A	N/A	7.65	4.6	N/A	6.48	8.545	1.737	4	28.80%	5.84
Endosulfan I	2.90	2.51	3.30	3.1	3.4	4.09	2.5	N/A	3.15	3.2	0.601	6	19.06%	4.03
Endosulfan II	15.15	16.88	13.80	13.7	14.8	N/A	13.5	N/A	14.53	13.80	1.395	5	9.80%	N/A
Oxychlordane	7.30	6.26	N/A	5.8 (13.5)	6.1 (14.1)	ND	N/A	N/A	4.54	5.95	3.033	4	66.80%	ND

* Original results submitted by Laboratory 9234 using Septum Programmable Injector (SPI). See individual lab review for detailed explanation.

(1) Results in brackets were original values reported by Laboratories 9233 and 9236. See individual lab reviews for detailed explanation.

(1, # "Corrected" results for Laboratory 9236. See individual lab review for explanation. # result excluded from statistical calculations

TABLE 3 - Results for IADN OC3 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
α -HCH	5.04	2.98	5.17	3.3	4.3	4.46	4.4	4.54 (1.077)	4.16	4.4	0.760	7	18.25%	5.00
γ -HCH	2.60	1.59	2.74	1.9	2.4	2.17	2.3	2.2095	2.19	2.2095	0.366	7	16.73%	1.88
p,p-DDT	11.52	11.81	14.46	10.8	11.2	9.96	11.3	9.431	11.28	11.2	1.622	7	14.38%	6.50
o,p-DDT	4.80	5.06	5.24	4.7	5.2	4.52	4.7	N/A	4.90	4.88	0.302	6	6.16%	4.03
p,p-DDD	14.28	15.09	13.91	12.3	13.7	11.55	13.6	18.406 (13.61)	14.08	13.7	2.225	7	15.80%	9.60
o,p-DDD	3.15	2.81	3.32	N/A	N/A	2.79	N/A	N/A	2.97	2.81	0.300	3	10.10%	2.29
p,p-DDE	5.10	4.90	4.64	4.5	6.2	5.55	4.8	6.411	5.29	4.90	0.774	7	14.64%	2.11
o,p-DDE	14.52	N/A	N/A	N/A	N/A	10.14	N/A	N/A	-	-	-	1	-	9.52
α -Chlordane	2.85	2.59	2.90	2.6	2.6	2.86	2.7	N/A	2.71	2.65	0.139	6	5.15%	2.16
γ -Chlordane	13.20	13.09	12.74	11.8	11.9	10.01	12.7	N/A	12.04	12.3	1.116	6	9.27%	8.46
Heptachlor Epoxide	5.10	5.06	5.24	4.6 (3.8)	5.3	5.02	5.1	N/A	5.05	5.08	0.247	6	4.88%	3.63
p,p-Methoxychlor	2.45	2.84	3.32	2.5	2.3	3.32	2.6	N/A	2.81	2.72	0.429	6	15.26%	ND
Dieldrin	12.96	13.97	12.33	11.5	12.5	9.46	11.4	13.028	12.03	12.33	1.435	7	11.93%	8.79
Hexachlorobenzene	5.30	4.73	4.69	5.6 (1.6)	6.0 (1.8)	4.25	5.4	6.017	5.24	5.4	0.893	7	13.22%	3.83
Endrin	2.80	4.97	3.03	N/A	N/A	4.05	2.4	N/A	3.61	3.54	1.132	4	31.33%	2.40
Endosulfen I	13.92	13.96	13.12	14.3	15.2	15.24	14.6	N/A	14.40	14.45	0.803	6	5.58%	16.56
Endosulfen II	5.05	5.87	5.34	4.8	5.2	N/A	4.7	N/A	5.18	5.2	0.468	5	9.04%	N/A
Oxychlordane	3.65	3.33	N/A	2.8 (5.4)	3.2 (7.4)	2.54	N/A	N/A	2.97	3.0	0.363	4	12.25%	3.48

TABLE 4 - Results for IADN OC4 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
α -HCH	12.08	9.38	11.69	9.1	10.4	9.88	10.2	12.11 (2.9365)	10.39	10.2	1.128	7	10.85%	11.00
γ -HCH	10.40	8.16	9.68	8.3	9.5	7.75	9.2	8.5015	8.73	8.5015	0.735	7	8.42%	7.03
p,p-DDT	16.32	16.99	20.06	16.1	16.1	15.12	13.5	10.05	15.42	16.1	3.097	7	20.09%	9.37
o,p-DDT	11.52	11.96	12.30	11.7	12.1	10.09	10.5	N/A	11.44	11.83	0.919	6	8.03%	8.78
p,p-DDD	20.23	20.87	20.37	18.5	19.5	17.01	19.7	28.0335 (16.514)	20.57	19.7	3.528	7	17.15%	12.81
o,p-DDD	12.60	11.46	11.30	N/A	N/A	9.52	N/A	N/A	10.76	11.30	1.077	3	10.01%	8.38
p,p-DDE	12.24	12.21	11.49	10.9	15.0	10.88	11.7	13.52	12.24	11.7	1.514	7	12.37%	5.79
o,p-DDE	20.57	N/A	N/A	N/A	N/A	15.07	N/A	N/A	-	-	-	1	-	13.13
α -Chlordane	11.40	10.66	10.65	10.4	10.8	9.22	10.5	N/A	10.37	10.575	0.561	6	5.60%	7.38
γ -Chlordane	18.70	18.38	18.12	17.2	16.8	14.72	17.7	N/A	17.15	17.45	1.328	6	7.73%	11.60
Heptachlor Epoxide	12.24	12.32	11.04	11.5 (11.6)	12.2	9.87	12.4	N/A	11.56	11.85	0.982	6	8.50%	7.32
p,p-Methoxychlor	9.80	11.71	12.64	10.3	9.6	14.79	10.2	N/A	11.54	11.005	1.944	6	16.85%	5.55
Dieldrin	18.36	20.57	17.39	16.8	17.8	13.88	15.8	18.525	17.25	17.39	2.107	7	12.21%	12.38
Hexachlorobenzene	12.72	11.84	10.08	13.6 (4.0)	14.5 (4.2)	9.43	13.2	16.015	12.67	13.2	2.366	7	18.68%	8.80
Endrin	11.20	18.28	11.05	N/A	N/A	14.04	9.3	N/A	13.17	12.545	3.930	4	29.85%	9.24
Endosulfen I	19.72	19.74	18.67	13.8	21.2	22.44	20.5	N/A	19.39	20.12	3.023	6	15.59%	22.85
Endosulfen II	12.12	14.14	11.98	11.6	12.1	N/A	11.0	N/A	12.16	11.98	1.185	5	9.74%	N/A
Oxychlordane	14.60	12.73	N/A	13.0 (27.0)	12.8 (29.1)	11.85	N/A	N/A	12.60	12.785	0.510	4	4.05%	12.80

* Original results submitted by Laboratory 9234 using Septum Programmable Injector (SPI). See individual lab review for detailed explanation.

() Results in brackets were original values reported by Laboratories 9233 and 9236. See individual lab reviews for detailed explanation.

[], # "Corrected" results for Laboratory 9236. See individual lab review for explanation. # result excluded from statistical calculations

TABLE 5 - Instruments and GC Columns

Lab Code	9231	9232	9233-HP	9233-V	9234	9235	9236
Instrument	GC/ECD: HP5890	GC/ECD: HP5890	GC/ECD: HP5890	GC/ECD: Varian 3400	GC/ECD: Vista 6000 *	GC/ECD: HP5890	GC/ECD: HP5890
Column	DB-5, 60 m DB-17	DB-1, 30 m DB-5, 30 m	DB-5, 60 m DB1701, 60 m	DB-5, 60 m DB1701, 60 m	DB-5, 60 m	DB-1, 30 m DB-5, 30 m	DB-5, 30 m

All participants received a set of ampoules prepared in iso-octane.

- This participant originally analyzed the ampoules using a Varian Star 3400 GC/ECD, a DB-5 60 m column, and a new SPI (Septum Programmable Injector). It was subsequently discovered that the SPI was not suitable for pesticide analysis. The ampoules were re-analyzed using the above analytical system.

TABLE 6 - Distribution of Participants Results

LAB ID CODE	9231		9232		9233-HP		9233-V		9234		9235		9236	
Target Range	n	%	n	%	n	%	n	%	n	%	n	%	n	%
<60%	2	2.9%	0	0.0%	0	0.0%	1	1.7%	2	2.9%	0	0.0%	0	0.0%
60-75%	2	2.9%	3	4.7%	5	8.3%	0	0.0%	7	10.3%	0	0.0%	1	3.6%
75-90%	15	22.1%	10	15.6%	20	33.3%	9	15.0%	28	41.2%	23	38.3%	7	25.0%
90-110%	36	52.9%	41	64.1%	35	58.3%	40	66.7%	16	23.5%	37	61.7%	8	28.6%
110-130%	9	13.2%	9	14.1%	0	0.0%	10	16.7%	6	8.8%	0	0.0%	10	35.7%
>130%	4	5.9%	1	1.6%	0	0.0%	0	0.0%	9	13.2%	0	0.0%	2	7.1%

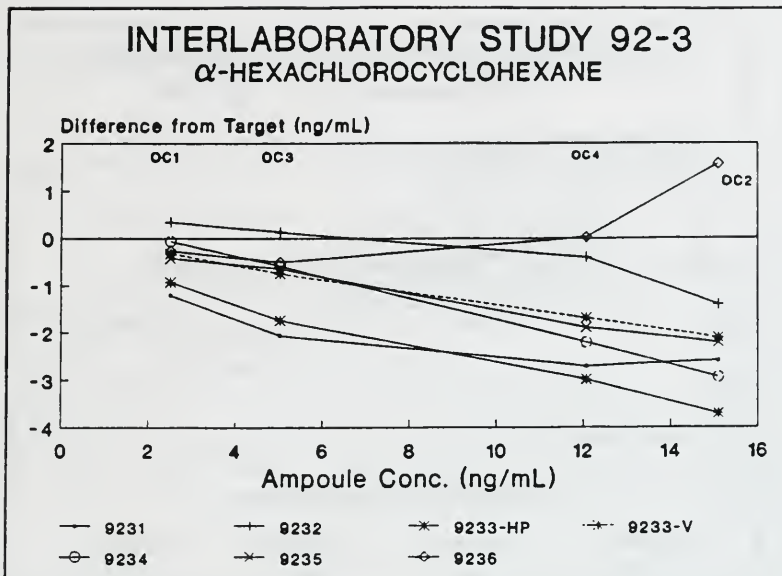


Figure 1 - Absolute Difference from Target

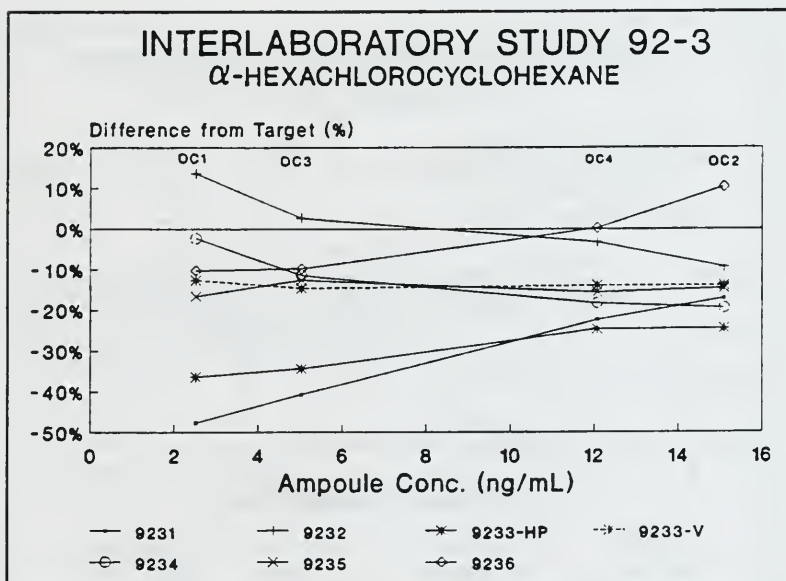


Figure 2 - Percent Difference from Target

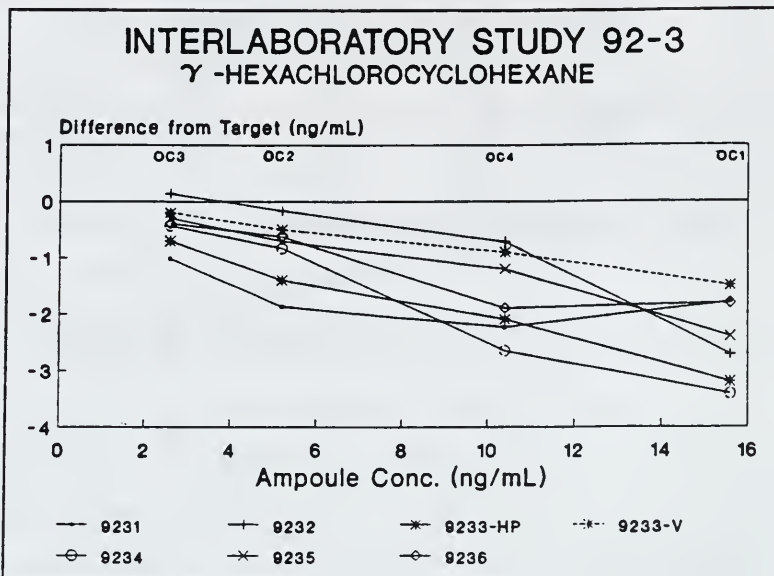


Figure 3 - Absolute Difference from Target

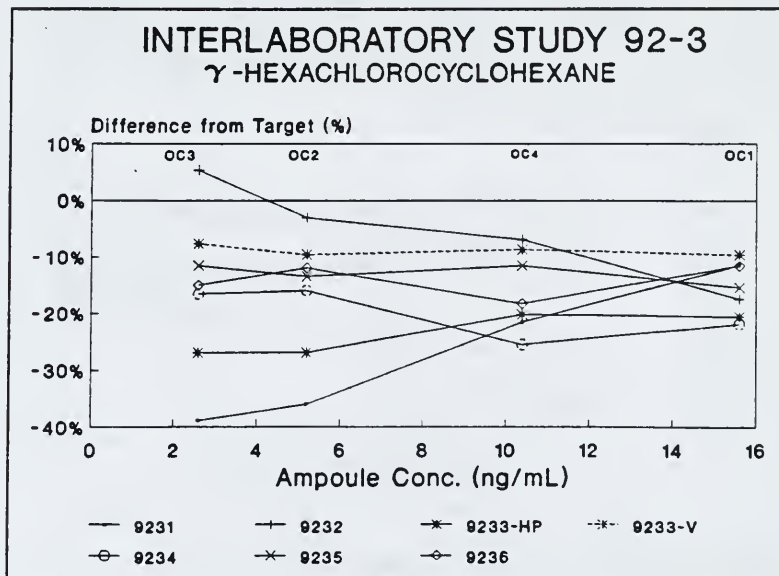


Figure 4 - Percent Difference from Target

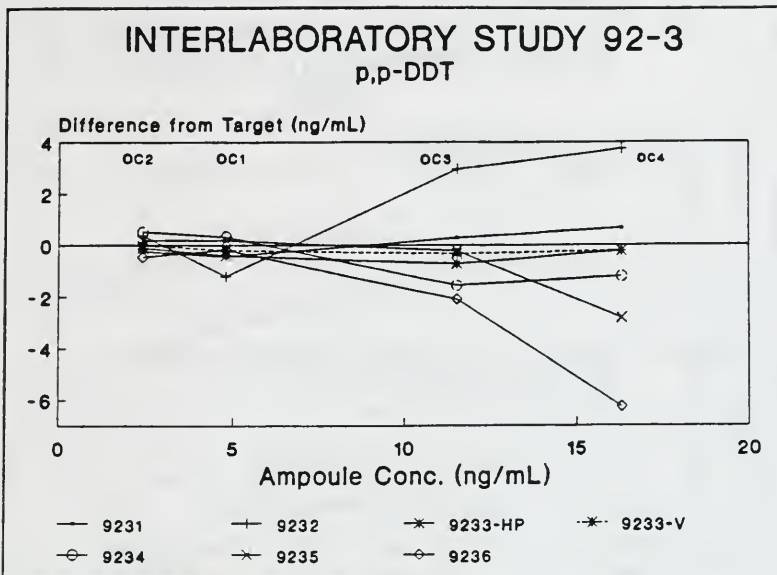


Figure 5 - Absolute Difference from Target

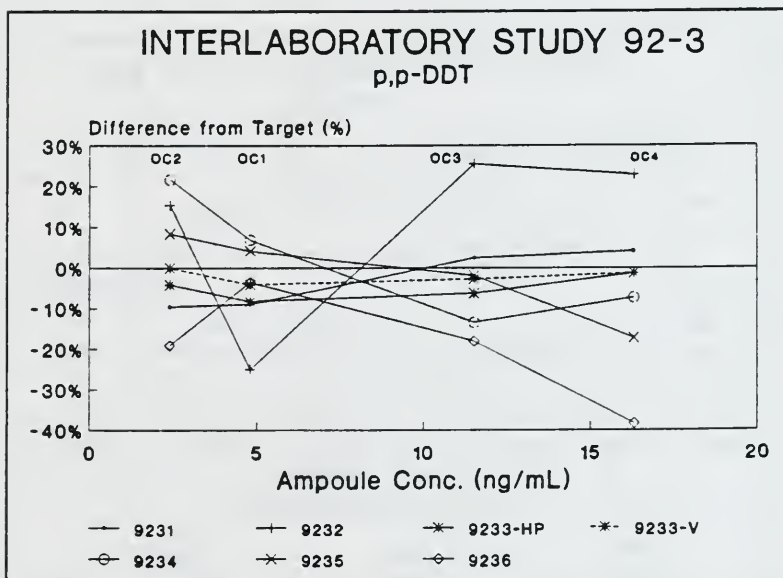


Figure 6 - Percent Difference from Target

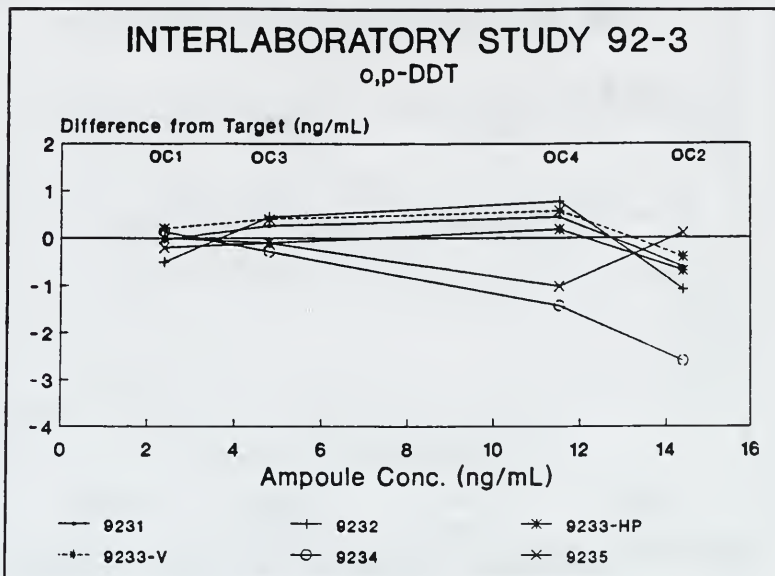


Figure 7 - Absolute Difference from Target

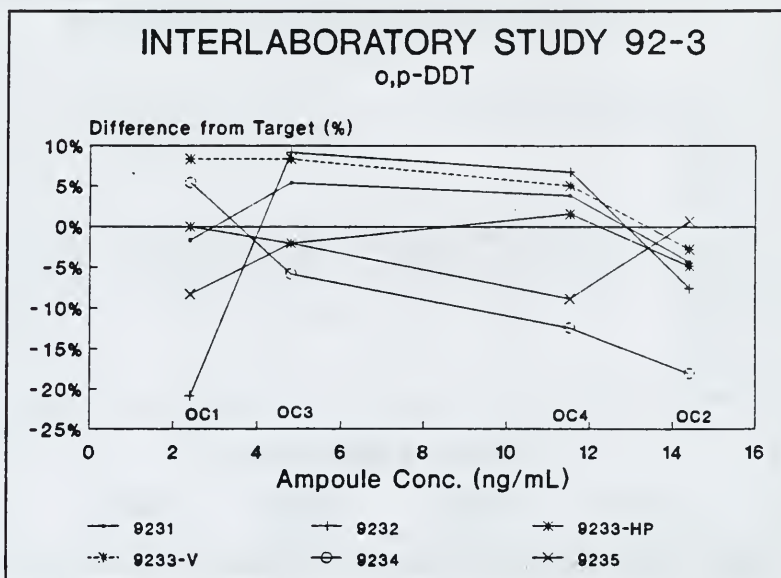


Figure 8 - Percent Difference from Target

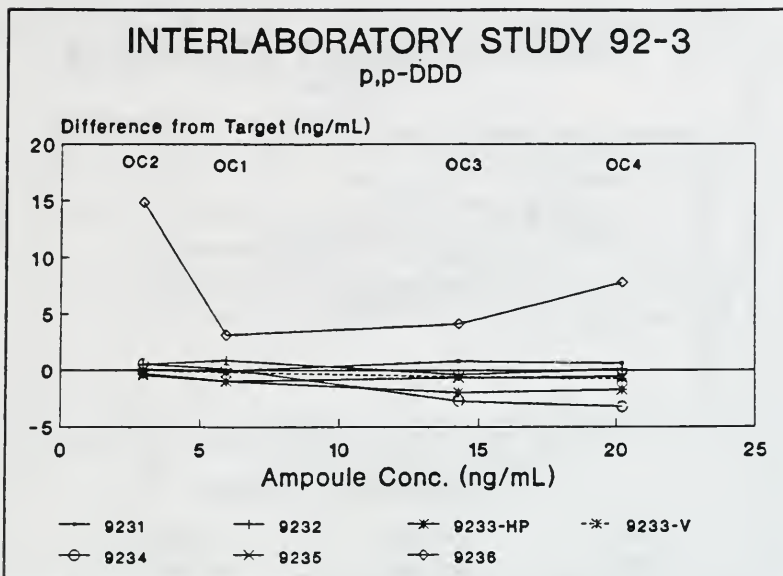


Figure 9 - Absolute Difference from Target

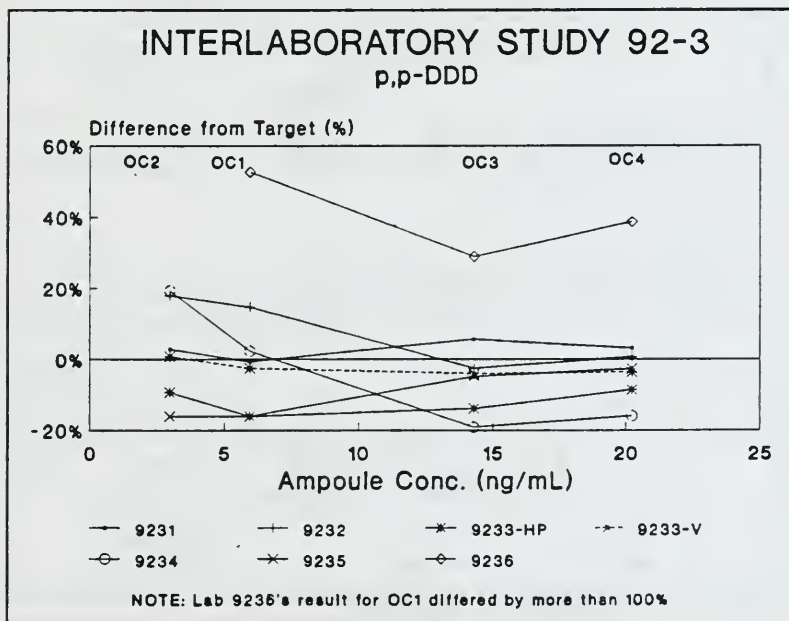


Figure 10 - Percent Difference from Target

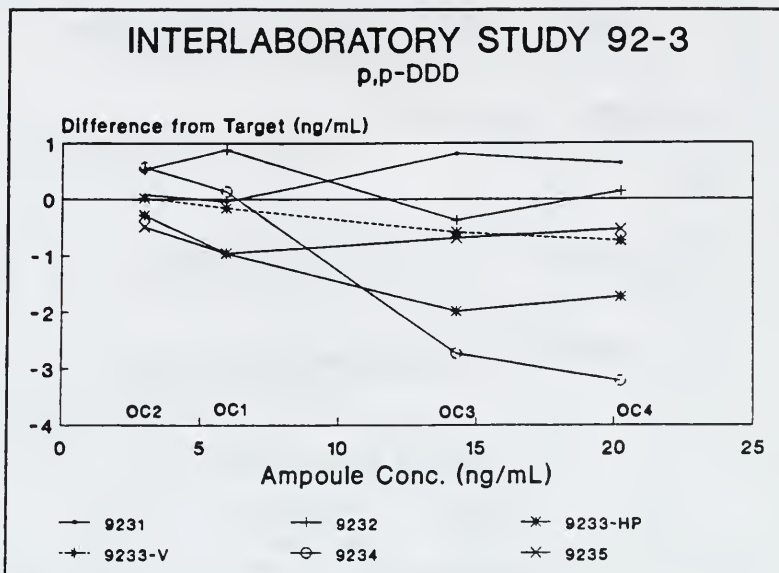


Figure 11 - Absolute Difference from Target

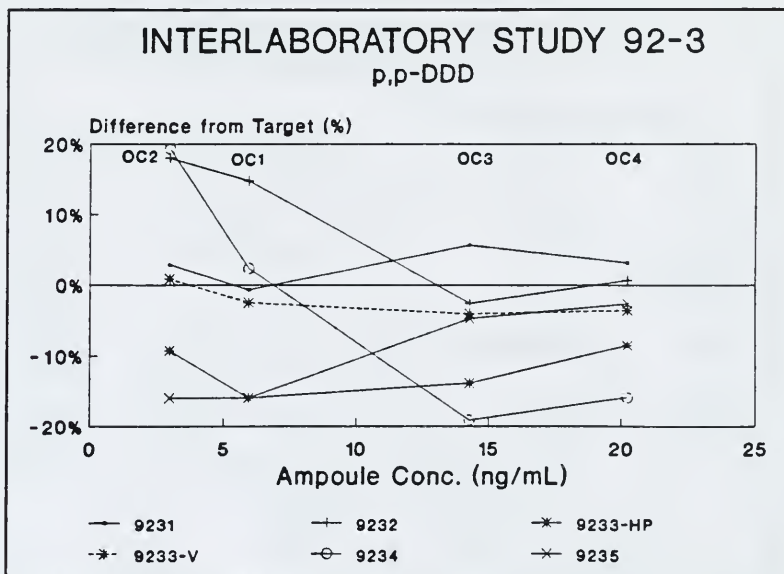


Figure 12 - Percent Difference from Target

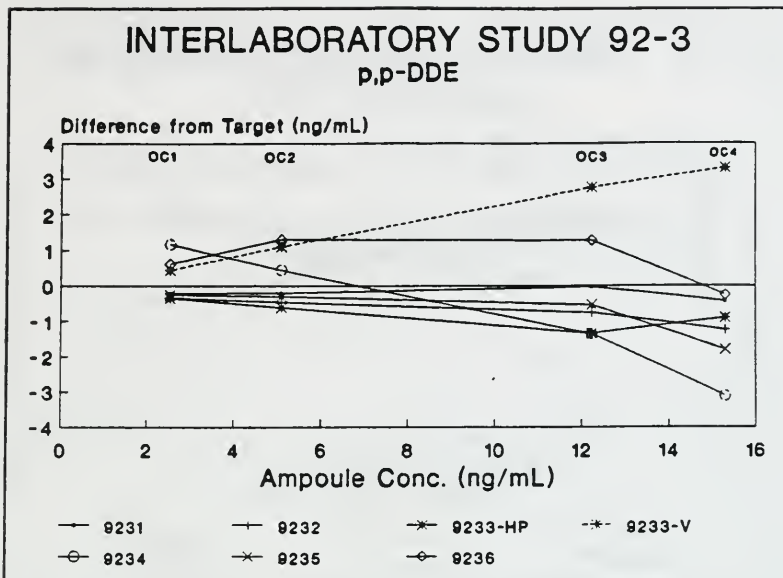


Figure 13 - Absolute Difference from Target

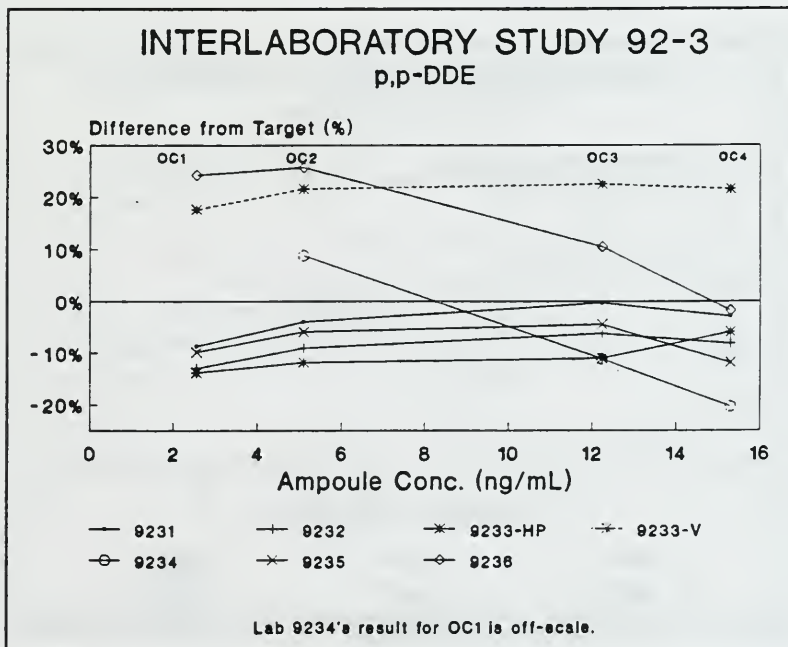


Figure 14 - Percent Difference from Target

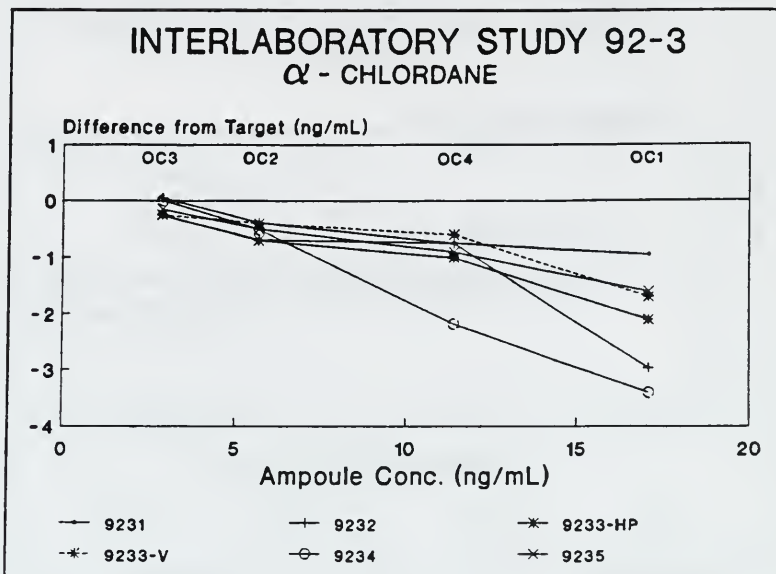


Figure 15 - Absolute Difference from Target

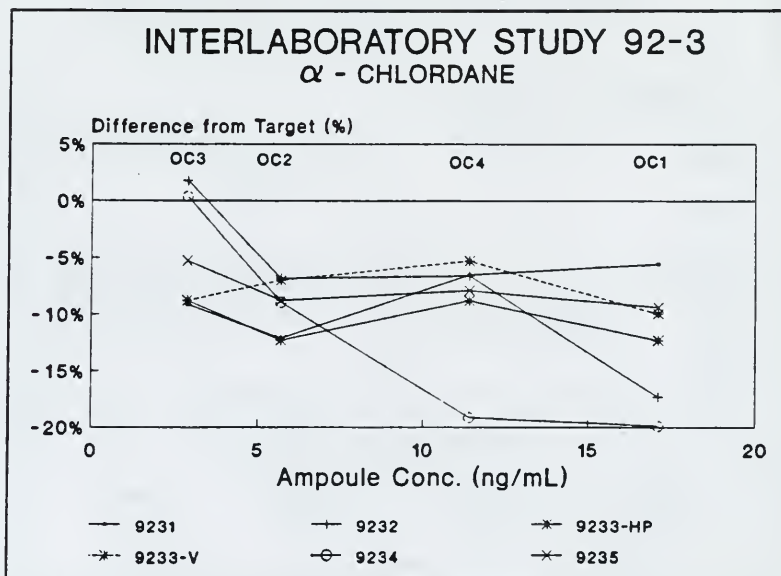


Figure 16 - Percent Difference from Target

INTERLABORATORY STUDY 92-3 γ -CHLORDANE

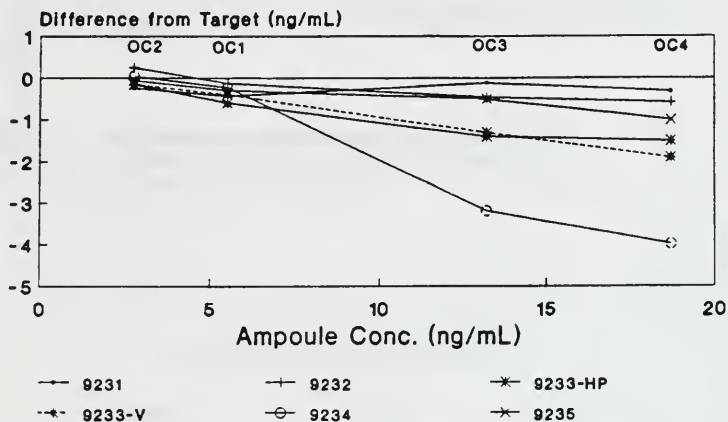


Figure 17 - Absolute Difference from Target

INTERLABORATORY STUDY 92-3 γ -CHLORDANE

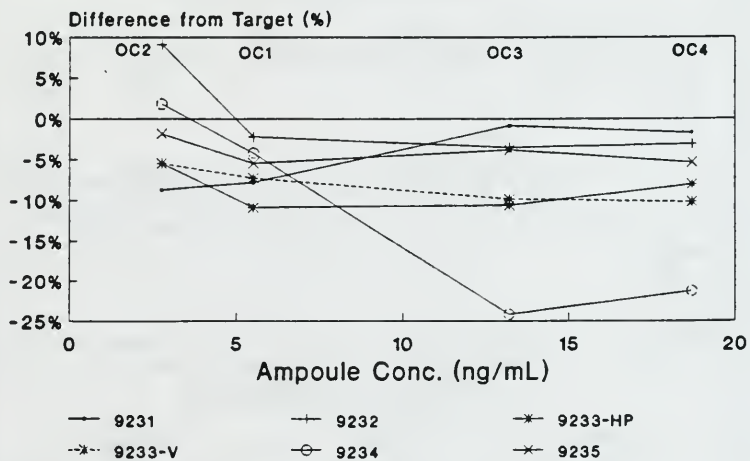


Figure 18 - Percent Difference from Target

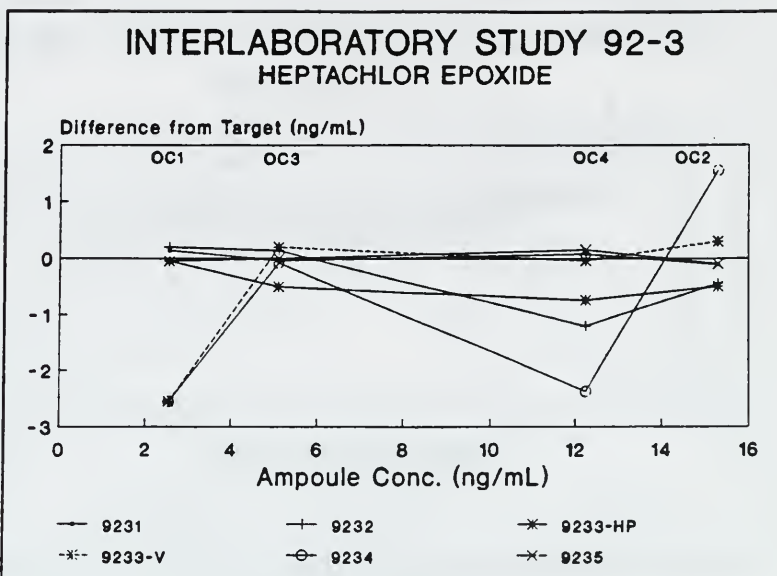


Figure 19 - Absolute Difference from Target

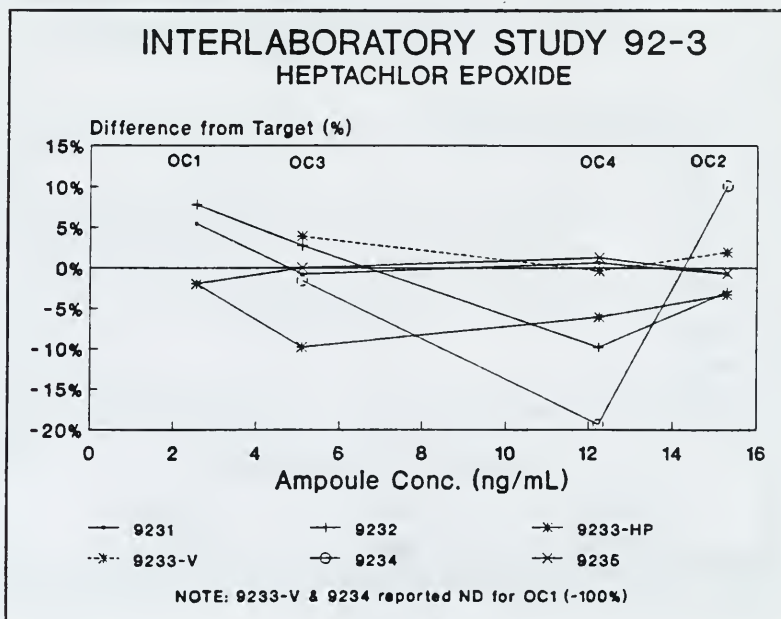


Figure 20 - Percent Difference from Target

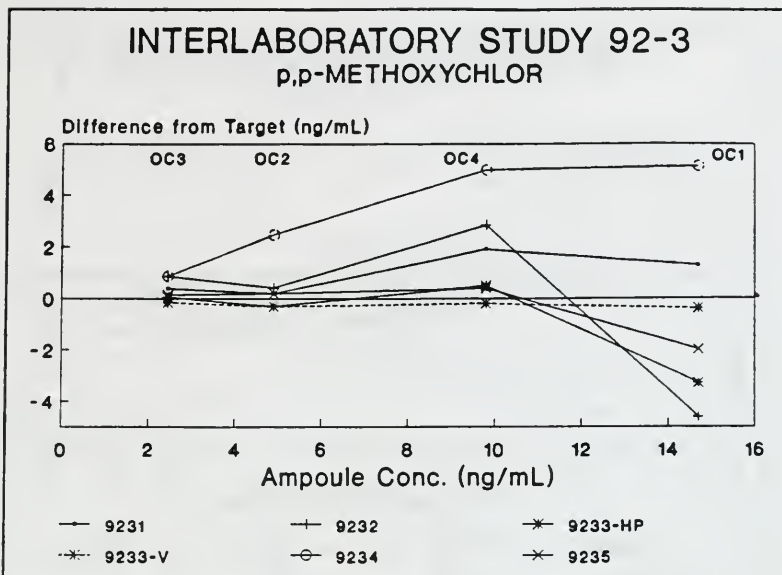


Figure 21 - Absolute Difference from Target

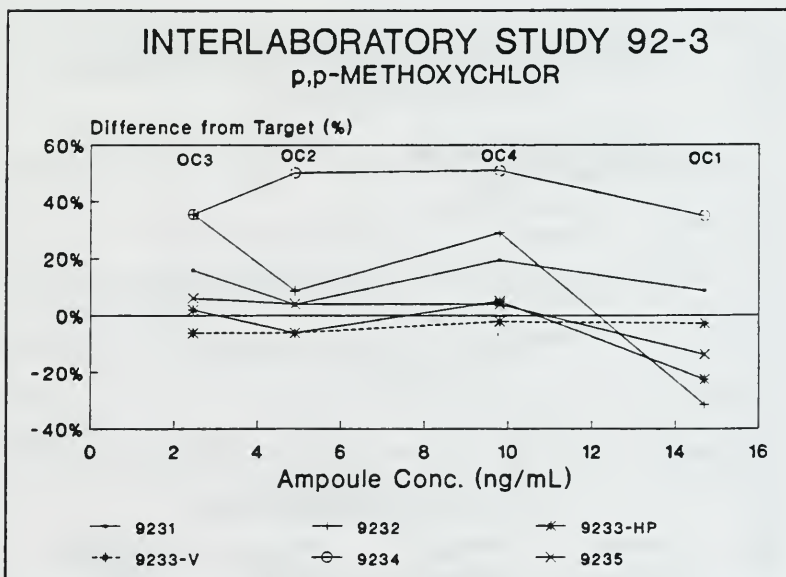


Figure 22 - Percent Difference from Target

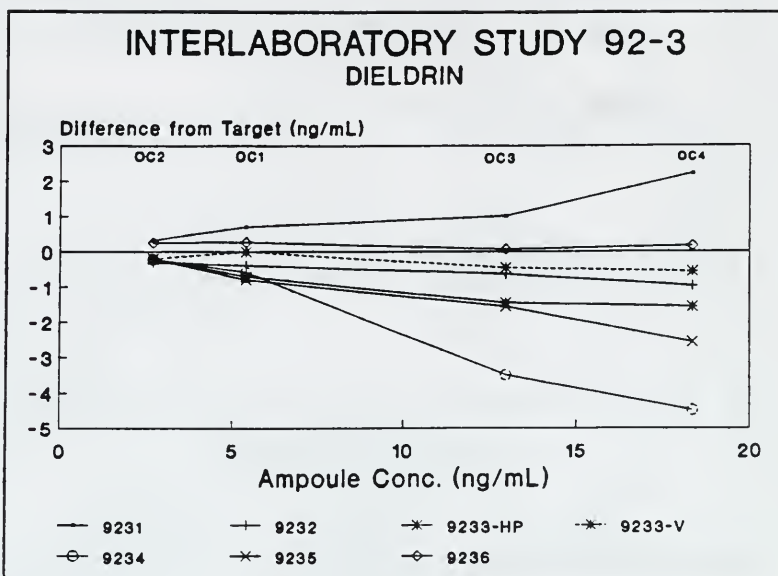


Figure 23 - Absolute Difference from Target

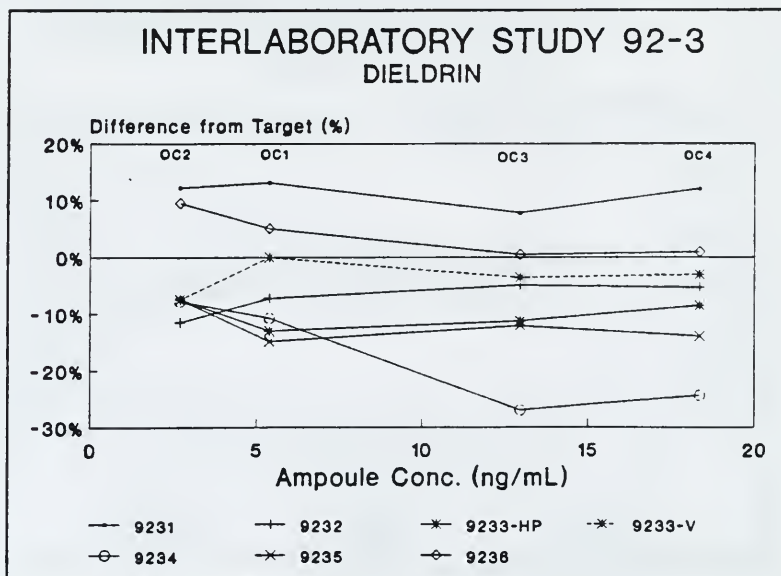


Figure 24 - Percent Difference from Target

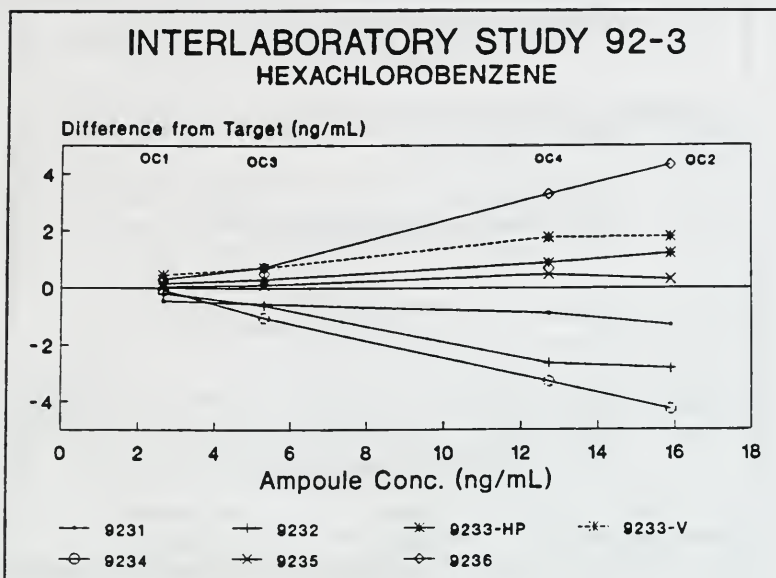


Figure 25 - Absolute Difference from Target

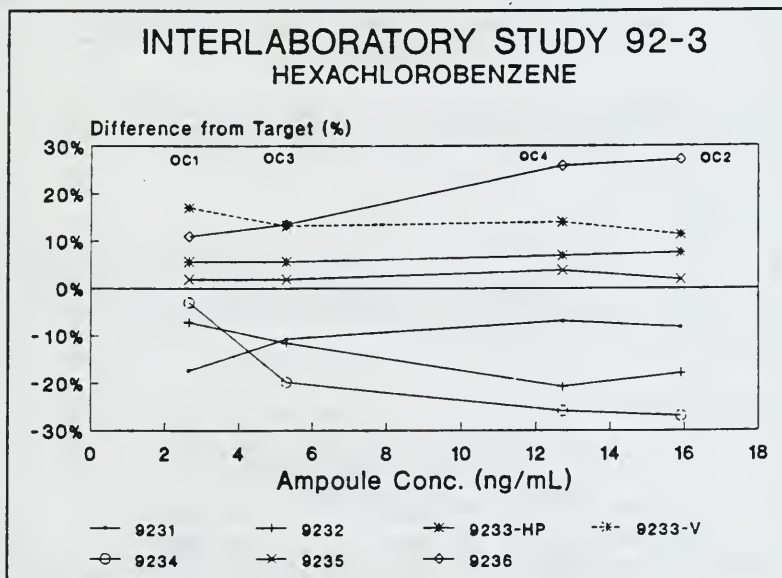


Figure 26 - Percent Difference from Target

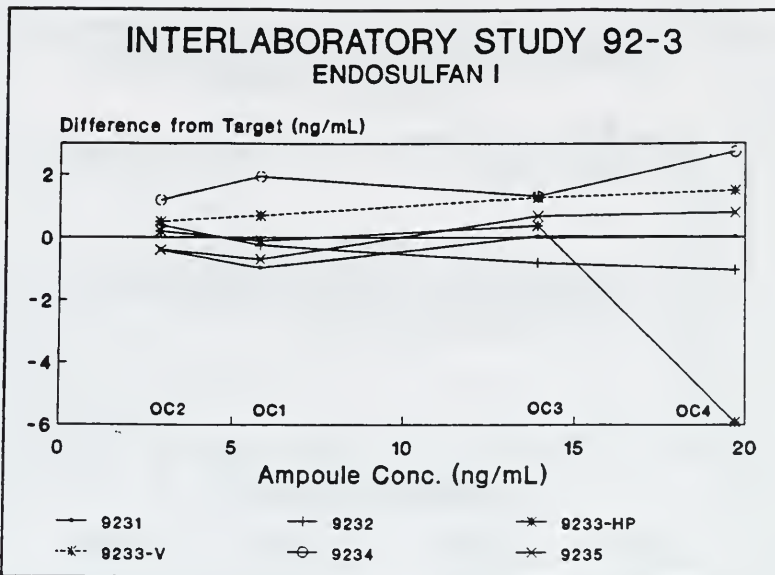


Figure 27 - Absolute Difference from Target

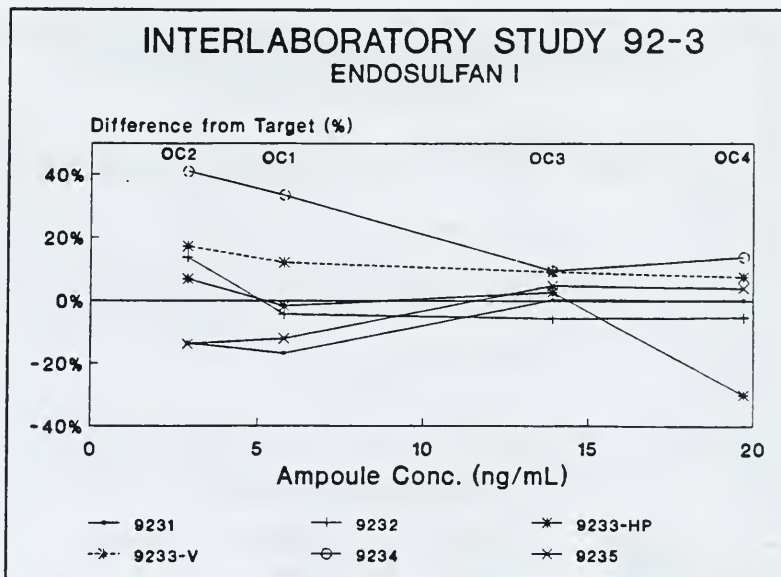


Figure 28 - Percent Difference from Target

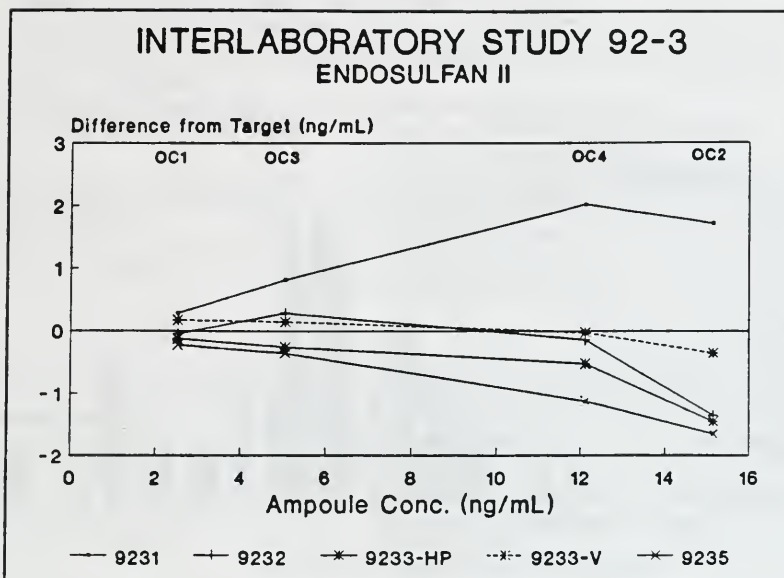


Figure 29 - Absolute Difference from Target

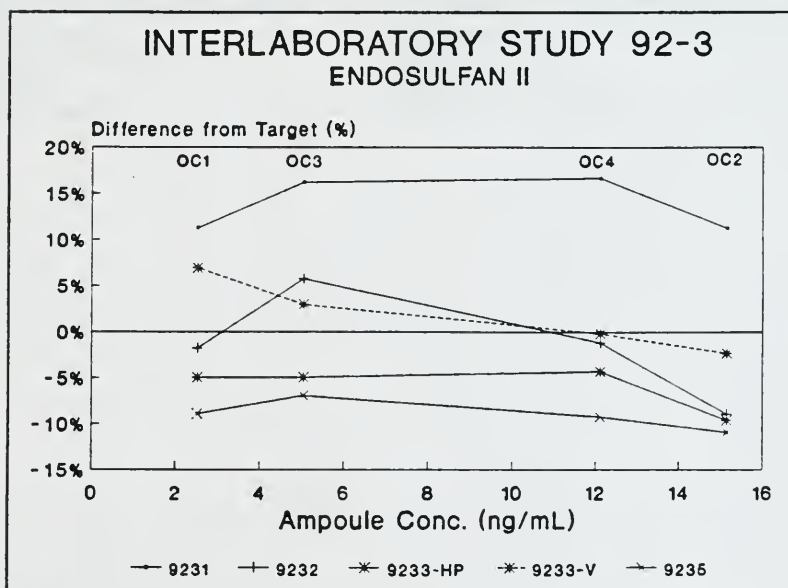


Figure 30 - Percent Difference from Target

INTERLABORATORY STUDY 92-3

Distribution of Participants' Results

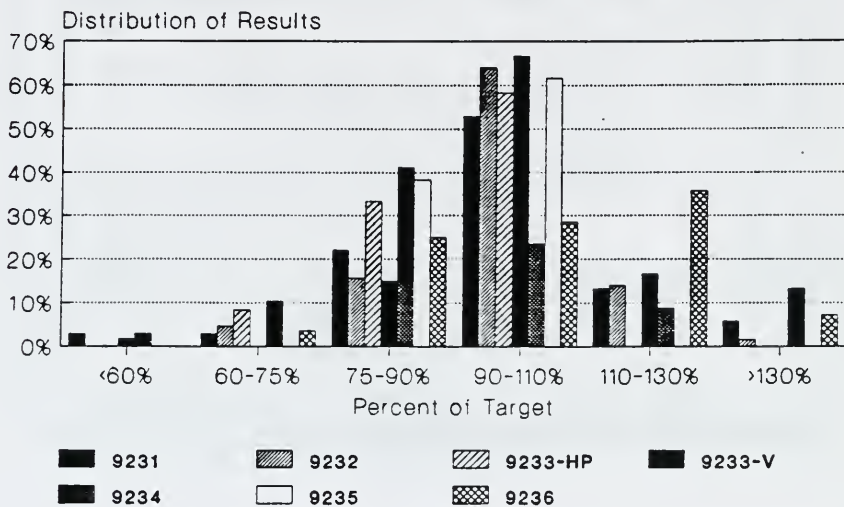


Figure 31 - Distribution of Participants' Results Relative to Target

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE**List of Participants**

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Burlington, Ontario
L7R 4A6
(905) 336-4775/6025

October 5, 1992

Dear Interlaboratory Study 92-3 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Organochlorine Pesticides (OC's). The ampoules are labelled IADN OCs 1, IADN OCs 2, IADN OCs 3, and IADN OCs 4. If you are missing any of the ampoules or they have broken in transit, please contact me at (416) 235-5842 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. The parameters present are indicated on the form.

Please report all results on the accompanying form by October 23, 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-3

OC's FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

PARAMETER	IADN OCs 1	IADN OCs 2	IADN OCs 3	IADN OCs 4
α -Hexachlorocyclohexane (α -HCH)				
γ -Hexachlorocyclohexane (γ -HCH)				
p,p-DDT				
o,p-DDT				
p,p-DDD				
o,p-DDD				
p,p-DDE				
o,p-DDE				
α -Chlordane				
γ -Chlordane				
Heptachlor Epoxide				
Methoxychlor				
Dieldrin				
Hexachlorobenzene (HCB)				
Endrin				
Endosulfan I				
Endosulfan II				
Oxychlordane				

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6107

January 15, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-3

Thank you for your participation in Interlaboratory Study 92-3 for the analysis of Organochlorine Pesticides (OC's) in ampouled standards. This study was in support of the Integrated Atmospheric Deposition Network (IADN) program. I apologize for the delay in reporting results, but one participant did not report their final results until this week.

The results are provided in the attached tables. Target values are provided. Please inform me of any transcription errors by January 29, 1993.

Each participant received a set of ampoules prepared from the same stock solution, prepared in iso-octane.

The Quality Assurance Working Group of the Canada-Ontario Agreement (COA) has been the directing force for these interlaboratory studies. They wish to know the identities of the participating laboratories for the purposes of data comparison for IADN. The Program Managers and Principle Investigators (U.S. and Canadian) for IADN also wish to have the laboratories identified. As the original invitation for this study indicated that laboratory codes were confidential, I am asking each participant to give me permission to reveal their identities to these groups of data users. Please notify me in writing with your permission to reveal your study code.

A date has not yet been set for the next set of ampouled standards in this series of IADN studies, but hopefully will take place in late February or in March. A letter will be sent out giving several weeks notice.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist

9 APPENDIX 3 - INTERPRETATION OF BIASES IN DIFFERENCE PLOTS

Interlaboratory study results may be evaluated by comparing the difference from target (D) to the target or consensus value (X). This may be graphically represented with the Difference (D) on the vertical axis and the Target or consensus value (X) on the horizontal axis. By joining the individual points for each participant in order of increasing concentration, imprecision (squiggle in the line) versus bias or curvature (location of line relative to its expected position) may be demonstrated.

The precision envelope for the difference plots may be described by the following equation:

$$D = B_i + B_s \cdot C \pm (DL + f \cdot C)$$

where:	D	Difference from target	B_i	Intercept Bias
	C	Concentration	B_s	Slope Bias
	DL	Detection Limit	f	Fluctuation factor

The fluctuation factor (f) for Organics is usually 10-20%. Data users' needs may determine how large a value for f is acceptable.

If there are no biases present (B_i and $B_s = 0$), the shape is symmetrical to and centred on the target line. Measurement differences among participating laboratories in an interlaboratory study should be attributable only to random fluctuation. An example using $DL = 5 \mu\text{g/L}$ and $f = 10\%$ is given in Figure 32.

When an intercept bias is present, the envelope shifts in the direction of the bias. If this shift exceeds the Method Detection Limit (MDL), this becomes a matter of concern for the analyst. An example with $B_i = -5 \mu\text{g/L}$ is given in Figure 34.

When a slope bias is present, the envelope broadens in the direction of the bias as concentration increases. When this bias exceeds the $MDL + 10\%$ concentration, it becomes a matter of concern for the analyst. An example of $B_s = +10\%$ is given in Figure 36.

Most interlaboratory study data sets will show a combination of slope and intercept biases among the participants. The precision envelope changes according to the magnitude of both effects. An example using $B_i = -5 \mu\text{g/L}$ and $B_s = +10\%$ is given in Figure 38.

The results may also be plotted using the relative difference (R) on the vertical axis. The precision envelope flares dramatically as the concentration approaches zero. This type of plot tends towards an exaggerated impression of unacceptable variability at the bottom end and may mask biases at higher concentration levels. However it can be useful when describing the range of performance among a group of participants. The above examples that were presented using concentration units (absolute scale) are also presented using a relative scale (Figures 33, 35, 37 and 39).

REFERENCE

King, D.E.; July 1993; *Interpretation of Interlaboratory Comparison (Round-Robin) Data*; Internal Report, Ministry of Environment and Energy, Laboratory Services Branch; Draft.

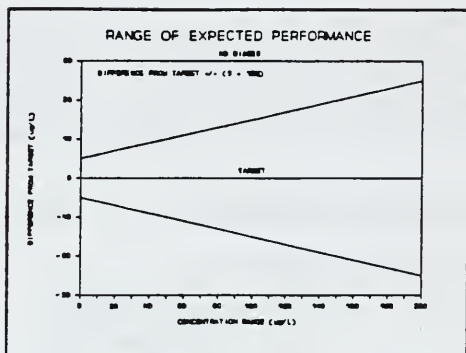


Figure 32 - Absolute Scale

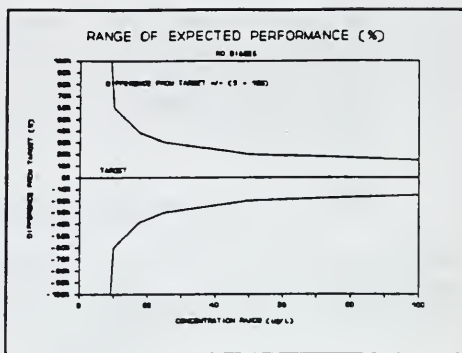


Figure 33 - Relative (%) Scale

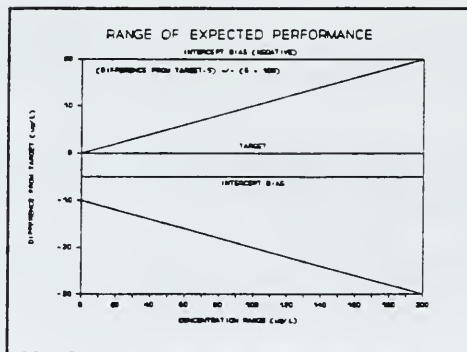


Figure 34 - Absolute Scale

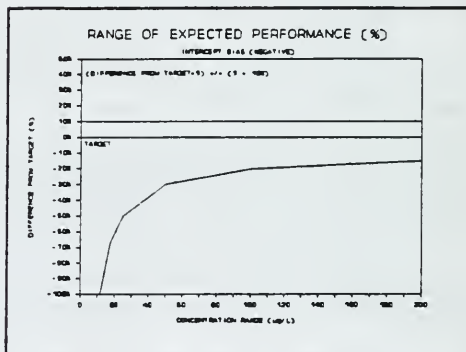


Figure 35 - Relative (%) Scale

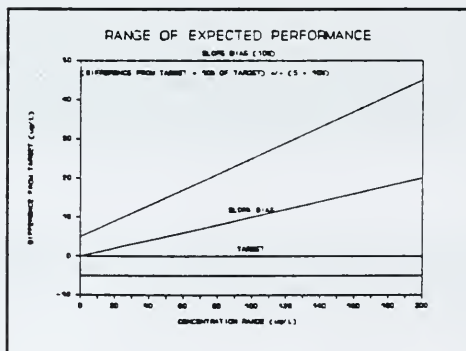


Figure 36 - Absolute Scale

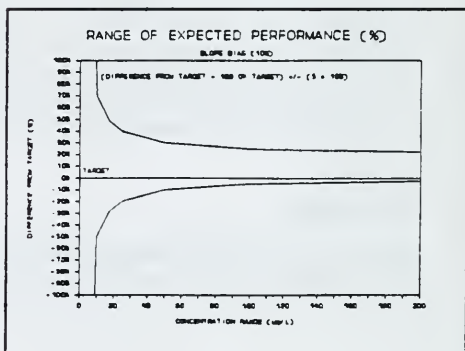


Figure 37 - Relative (%) Scale

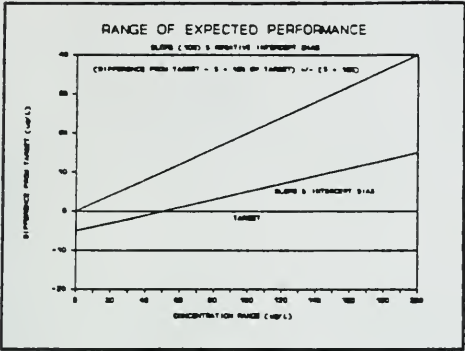


Figure 38 - Absolute Scale

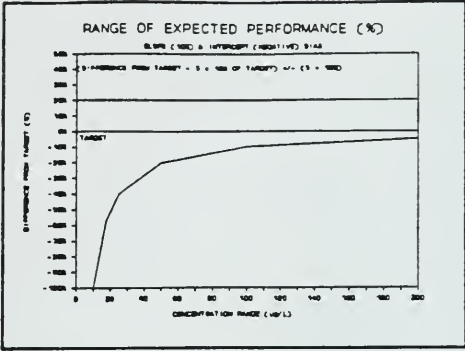


Figure 39 - Relative (%) Scale

